

A Further Study
—OF THE—
Products Formed by the Action of Heat
on Parasulphaminebenzoic Acid.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

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W. B. STODDARD

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ACKNOWLEDGMENT.

The author of this work wishes to express his sincere thanks to Prof. Remsen, at whose instigation and under whose personal supervision, it was carried out. He desires also to express his appreciation of the instruction received from Prof. Morse and Prof. Clark.

A FURTHER STUDY OF THE PRODUCTS FORMED BY THE ACTION OF HEAT ON PARA- SULPHAMINEBENZOIC ACID.

INTRODUCTION.

In 1894, Hartman, working in this laboratory on the action of heat on parasulphaminebenzoic acid, made among others, the following observations :¹ (1) If heated to 285° the acid is converted into a perfectly soluble compound, which he showed to be the acid ammonium salt of parasulphobenzoic acid. (2) If heated to 235° no loss in weight occurs, the products being, however, only partially soluble.

In 1895, Muckenfuss,² also working in this laboratory, took up the work at this point. From the mass obtained by heating parasulphaminebenzoic acid to 220° for eight hours he isolated the following substances : Free parasulphobenzoic acid, the acid ammonium salt of parasulphobenzoic acid, an insoluble and infusible substance which he refers to as the "infusible diamide of parasulphobenzoic acid," and an acid which he describes as isoparasulphaminebenzoic acid.

For the sake of comparing the infusible diamide with the ordinary variety, the latter was prepared by the following two methods : (1) Parasulphaminebenzoic acid was converted into the acid ammonium salt by heating with hydrochloric acid in a sealed tube ; from this the neutral potassium salt was obtained, which gave the chloride on treatment with phosphorus pentachloride. From the chloride, the diamide was formed in the usual manner. (2) Parasulphaminebenzoic acid was converted into the chloride, which was then treated with ammonia. Both these methods gave the same substance which crystallizes in needles and melts at 230° . It is soluble in dilute caustic soda, from which solution one atom of nitrogen is given up as ammonia on boiling, the sodium salt of parasulphaminebenzoic acid being formed.

¹ Dissertation, p. 29.

² Dissertation, or Am. Chem. J., 18, 349.

The infusible diamide crystallizes in plates, and is soluble in dilute caustic soda. Instead of losing one atom of nitrogen as ammonia on boiling, both are given off, the neutral sodium salt of parasulphobenzoic acid being formed.¹ Both the diamides yield the acid ammonium salt of parasulphobenzoic acid when heated with hydrochloric acid in a sealed tube at 200°.

From the alcoholic extract of the mass resulting from the fusion of parasulphaminebenzoic acid at 220° for eight hours, Muckenfuss obtained flakes of a substance which proved to be an acid. He made and analyzed the barium salt, and found it to contain an acid isomeric with parasulphaminebenzoic acid, which he called isoparasulphaminebenzoic acid. The barium salt yielded the potassium salt of parahydroxybenzoic acid on heating with concentrated caustic potash.

This was about the condition of affairs when the present work was taken up.

Preparation of Material.

It was at first thought that possibly the formation of the infusible diamide and the iso acid might be due to the impurities which are known to exist in parasulphaminebenzoic acid, derived from commercial saccharine. An attempt was made to purify the acid from this source by repeated crystallization. 220 grams of the acid obtained from commercial saccharine were subjected to repeated crystallization from hot water. In no case did the crystals come out colorless, but always had a slightly brownish tinge. The crystallization was repeated seven times with the same result. The melting-points of the different crystallizations were neither constant nor sharp. They seem to vary with the time taken in heating the melting-point bulb.

After the seventh crystallization it was decided to use the substance synthetically prepared by the method devised by Remsen.² As an additional precaution, the crude parasulphaminebenzoic acid, obtained by the oxidation of paratoluene-sulphonamide, was dissolved in sodium carbonate, the unoxi-

¹ Am. Chem. J., 18, 356.

² Ann. Chem. (Liebig), 178, 297.

dized amide filtered off, the acid precipitated by hydrochloric acid, and finally purified by crystallization from water. Thus prepared, the acid is perfectly white and pure.

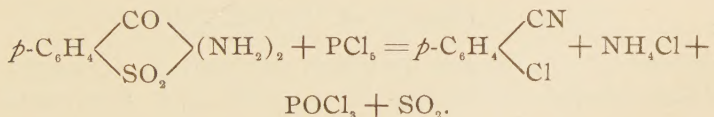
Portions of this product, which had been perfectly dried, were heated to 220° , as described by Muckenfuss. The same sublimes appeared, and the molten mass had the same general appearance as stated by him. On treatment of the product with water, an insoluble substance remained, which was purified by the method devised in the previous work.¹

Properties of the Infusible Diamide.

It is infusible and insoluble in alcohol, ether, chloroform, benzene and ligroin. It is slightly soluble in hot water, coming out in glistening plates on cooling. It is unattacked by boiling concentrated hydrochloric acid, and apparently by nitric acid, although it is soluble in this reagent. It is soluble in cold concentrated sulphuric acid, and the solution is not decomposed at 200° . It is unattacked by carbonates in the cold, but sodium carbonate liberates ammonia on boiling.² In all these respects it is identical with the substance obtained by Muckenfuss.

Action of Phosphorus Pentachloride on the Infusible Diamide.

In the previous work it was stated that there is no reaction between these substances at 200° . It was found that on heating a specimen of the diamide with phosphorus pentachloride, parachlorbenzonitrile is formed at 194° – 197° . It was identified by its odor, volatility with water vapor, its melting-point (94°), and the formation of crystals from alcohol and benzene solutions, agreeing in every respect with the compound described by Remsen and Dohme.³ The reactions may be expressed as follows :



¹ Am. Chem. J., 18, 353.

² This Dissertation, p. 9.

³ Am. Chem. J., 11, 347.

The reaction is very clean, a large yield of the chlorbenzonitrile being obtained.

Action of Hydrochloric Acid on the Infusible Diamide.

In the former work it was found that sodium hydroxide would set free all of the nitrogen of the diamide as ammonia, even at 0° . The conclusion drawn was that in the diamide both the nitrogen atoms bear the same relation to the molecule. It was thought that by using different agents one of the nitrogen atoms might be removed, leaving the other, and that from a study of the compounds thus formed, something might be deduced as to the structure of the diamide itself.

The first attempts were made with hydrochloric acid of varying concentrations and under different pressures.

In the first experiment fifth-normal acid was used at atmospheric pressure. The diamide was boiled for several hours, but no change could be detected. Then acid of specific gravity 1.12 was tried under the same conditions. After boiling for several days, a small amount of the acid ammonium salt of parasulphobenzoic acid, together with ammonium chloride, was found in the solution. A second portion was similarly treated for a week, but the amount of parasulphobenzoic acid which was recognized by its characteristic acid barium salt, was not appreciably increased. This long continued boiling with dilute hydrochloric acid renders the crystals of the diamide much larger than they were at first.

Another sample was heated with concentrated hydrochloric acid in a closed vessel at 100° without appreciable result. Reference has been made to the heating at 200° in a sealed tube. From these experiments it appears that it is impossible to hydrolyze one amido group with hydrochloric acid.

Attempts to Diazotize the Infusible Diamide.

A specimen of the diamide which was partially in suspension and partially in solution in sulphuric acid, was treated in the cold with a solution of sodium nitrite. Apparently no nitrous acid was consumed. The solution was gradually

heated, finally to boiling, fresh portions of the nitrite being added from time to time. The diamide crystallized out unchanged on cooling. A similar experiment was made, using nitrous fumes instead of the nitrite solution. This also failed to attack the diamide. This made it evident that neither of the amido groups could be removed in this way.

Action of Sodium Carbonate on the Diamide.

The action of bases weaker than caustic soda was next taken up, in the hope that only one of the nitrogen atoms would be liberated. To this end a weighed amount of the diamide was placed in a flask containing a solution of the base, the flask connected with a tin-tube condenser, and a current of steam, which was free from ammonia, was passed through. The distillate was caught in a measured volume of standard acid, by titrating the excess of which the ammonia liberated could be easily calculated. In the case of sodium carbonate, the saponification proceeded much more slowly than if sodium hydroxide had been used, but a point was soon reached when more than one-half of the nitrogen had been given off as ammonia. This showed that sodium carbonate would not accomplish the desired end, and the experiment was discontinued. Evidently a still weaker base must be used.

Action of Magnesium Hydroxide.

This was prepared by adding caustic soda to an excess of magnesium sulphate solution. Any carbonate present would be thrown down as magnesium carbonate, and the excess of magnesium sulphate present and the sodium sulphate formed, being neutral, might not be expected to interfere with the reaction. A preliminary experiment showed that this was true in the case of magnesium sulphate.

The first experiment gave the following results: Sulphuric acid was standardized by weighing as barium sulphate, and by titrating against a standard solution of ammonia, using methyl orange as an indicator. A solution of caustic soda (from the metal) was then titrated against this acid.

1 cc. acid = 28.124 mg. H_2SO_4 .

1 cc. acid = 2.122 cc. alkali.

1 cc. alkali = 10.82 mg. alkali.

0.1700 gram diamide gave the following :

Acid used, 22.43 cc.

Alkali used for excess of acid, 44.57 cc.

Acid used is equivalent to 47.60 cc. alkali.

Alkali equivalent of ammonia liberated, 3.03 cc.

Alkali equivalent to total nitrogen as ammonia, 6.28 cc.

The amount of ammonia liberated is equivalent to one-half of this within the limits of error. The ammonia was distilled over in five portions, coming off fairly rapidly at first, but soon coming so slowly that one and one-half days were required to complete the operation.

The experiment was repeated, using a larger amount of the diamide, and an attempt was made to isolate the soluble magnesium salt formed. The larger amount of magnesium sulphate and sodium sulphate present prevented this, as all the constituents are either soluble or insoluble in the ordinary solvents. In order to overcome this difficulty, pure magnesium hydroxide was precipitated from an excess of magnesium sulphate by caustic soda and the precipitate washed by decantation until barium chloride indicated that only a trace of sulphates were present.

The diamide was treated with this mixture, and steam passed through, as before. It was observed that as the reaction went on, the magnesium hydroxide went largely into solution. When the distillate came over neutral the operation was discontinued, and the excess of magnesium hydroxide filtered off. On evaporating the clear colorless solution nearly to dryness, diamond-shaped crystals, which, when perfect, were clear and colorless, separated out. They were found to contain magnesium, giving a precipitate with caustic soda. On boiling with concentrated caustic soda, ammonia is liberated, a salt of parasulphobenzoic acid being formed, which was recognized by its characteristic acid barium salt.

On the other hand, sodium carbonate does *not* liberate ammonia on boiling, or at least so slowly that the ammonia cannot be detected in a test-tube experiment. This is not what

might be expected, for sodium carbonate liberates *all* the nitrogen from the diamide as ammonia.

Properties of the Magnesium Salt.

It is very soluble in hot water, the solution requiring some time to become saturated. From a sufficiently concentrated solution, the salt crystallizes out slowly on cooling. Its solution has a slightly bitter taste.

If hydrochloric acid is added to a concentrated solution of the magnesium salt, *no* precipitate is formed, showing conclusively that it is not a salt of parasulphaminebenzoic acid, as this acid would be precipitated under the conditions.

Again, if barium chloride is added to a solution of the salt, no precipitate is formed, showing (1) that no sulphates or sulphites were formed during the decomposition of the diamide; and (2) that it is not a salt of the iso acid which would be precipitated as its barium salt. The acid forms soluble salts with silver, lead, mercuric mercury, copper, and ferric iron.

Analysis of the Magnesium Salt.

For the purpose of analysis, two specimens were prepared. The first was the second crystallization of the material which separated out from the solution of the magnesium salt which had been concentrated by evaporation. The second consisted of the crystals which separated on evaporating the combined mother-liquors. The crystals of both specimens were well formed. They were dried on paper, and by standing in the air, during which time they lose part of their water, becoming opaque.

First specimen :

1.4730 gram lost 0.2144 gram H_2O at 135° .

0.1820 gram gave 0.0178 gram MgO .

Second specimen :

0.6294 gram lost 0.0926 gram H_2O at 135° .

0.2040 gram gave 0.0200 gram MgO .

The salt may be heated to 275° without further loss.

Specimen.	H_2O .	MgO .
I	14.56	9.78
II	14.71	9.80

These figures are sufficient to show the identity of the two specimens, and from this we may infer that this salt is practically the only substance besides ammonia formed in the decomposition.

Analyses for sulphur and nitrogen gave the following results :

0.1660 gram gave 0.1858 gram BaSO_4 .

0.1500 gram gave 0.1652 gram BaSO_4 .

The nitrogen was determined by treating the salt with a large excess of caustic potash, passing steam through the hot solution, and titrating the ammonia liberated.

0.6097 gram gave ammonia equivalent to 10.68 cc. caustic soda solution containing 0.01082 gram NaOH per cubic centimeter.

0.4621 gram gave ammonia equivalent to 8.27 cc. of the same solution.

		Calculated for $(\text{C}_6\text{H}_4\text{COO}\text{SO}_2\text{NH}_2)_2\text{Mg} + 4\text{H}_2\text{O}$.		Found.			
H_2O		I4.52		I.		II.	
				I4.56		I4.71	
		Calculated for $(\text{C}_6\text{H}_4\text{COO}\text{SO}_2\text{NH}_2)_2\text{Mg}$.		Found.			
		I.	II.	III.	IV.	V.	VI.
Mg	5.66	5.87	5.88				
N	6.60			6.63	6.77		
S	15.09					15.37	15.11

From these results it is clear that the substance is a salt of an acid isomeric with parasulphaminebenzoic acid, and at the same time entirely different from the compound described as isoparasulphaminebenzoic acid in the former work.

The Potassium Salt.

The potassium salt was next studied. It was made by precipitating the magnesium from the magnesium salt by potassium carbonate, a solution of which was added gradually to a solution of the magnesium salt until no more precipitate was formed.

On filtering and boiling a second precipitate of magnesium carbonate was formed, which was filtered off. The explanation of the formation of this second precipitate is unknown.

On evaporating to the proper concentration, fine crystals of the potassium salt were formed. These were clear and colorless, and even in the small amount prepared, thick crystals, over a centimeter long, were formed. The crystal faces were too indistinctly developed to determine the crystal form. The potassium salt is very soluble, but not quite so much so as the magnesium salt. The following analytical results were obtained: On heating to 308° , the salt did not lose weight, nor show any signs of decomposition.

0.1505 gram gave 0.1468 gram BaSO_4 .

0.1563 gram gave 0.0574 gram K_2SO_4 .

0.2030 gram gave 0.0737 gram K_2SO_4 .

0.3496 gram gave ammonia equivalent to 5.56 cc. NaOH solution (1 cc. = 0.01082 gram NaOH).

	Calculated for $\text{C}_6\text{H}_4\text{CONH}_2\text{SO}_2\text{OK}$	Found.			
		I.	II.	III.	IV.
K	16.32	16.28	16.46		
S	13.39			13.43	
N	5.86				6.02

Action of Phosphorus Pentachloride on the Potassium Salt.

In order to determine whether the infusible diamide could be regenerated from the potassium salt, the latter was first treated with phosphorus pentachloride.

Reaction takes place very easily at a temperature slightly above the ordinary. On treatment with water, the product formed by the pentachloride breaks up into a pulverulent form, no apparent reaction between it and the water taking place. Indeed, it may be boiled with water without going into solution, or losing its characteristic appearance. It is comparatively insoluble in the organic solvents with the exception of alcohol, in which it is very soluble, and from which it may be crystallized. This solution may be boiled without decomposition. Ammonia dissolves the substance readily with evolution of heat, ammonium chloride being formed during the reaction. The extreme solubility of the substance shows that it is *not* the infusible diamide.

Discussion of Results.

The acid, whose salts have just been described, is clearly isomeric with parasulphaminebenzoic acid. Paracarbaminebenzenesulphonic acid would be such a compound. The fact that phosphorus pentachloride reacts with the potassium salt at a low temperature, is certainly not unfavorable to this view. Also the formation of ammonia on boiling with caustic soda indicates this structure, for parasulphaminebenzoic acid, in which the nitrogen is unquestionably in combination with sulphur, does not react in this manner. This would lead to the assumption that in the infusible diamide, both nitrogen atoms are in combination with carbon. As these are the only facts available, the whole question still remains an open one.

The Iso Acid.

This substance is obtained in flakes from the alcoholic extract of the mass resulting from the fusion of parasulphaminebenzoic acid at 220° for eight hours. On dissolving these flakes in water, rendering alkaline with ammonia, and adding barium chloride, the characteristic barium salt described by Muckenfuss is obtained. This can be purified by treatment with animal charcoal, boiling for a few minutes and crystallizing. The large amount of charcoal and the long continued boiling mentioned in the previous work, were found to be unnecessary.

Formation of the Acid from the Barium Salt.

The pure barium salt thus obtained was treated with the calculated amount of standard sulphuric acid, the barium sulphate filtered off, and the filtrate evaporated first over a free flame, and finally on a water-bath. As the solution becomes concentrated, no crystals appear, but as the evaporation approaches completion, the acid forms a thick, gummy skin over the surface of the liquid. The layers deposited on the sides of the dish become lemon-yellow in color when the breath is blown upon them, or when they are protected in any way from the water-vapor from the bath. This color disap-

pears when the vapors come in contact with the substance again. This is characteristic of the iso acid.

Properties of the Iso Acid.

The acid thus prepared is lemon-yellow throughout when dry. It is deliquescent, becoming pasty on standing in the air. On treatment with water it goes easily into solution, the yellow color disappearing as soon as the water comes in contact with it. From a fairly concentrated water solution, alcohol precipitates the acid in very minute crystals, which settle in flakes. The solution is acid toward litmus and has a sharp sour taste.

Action of Concentrated Hydrochloric Acid on the Iso Acid.

About one-half gram of the iso acid was heated with concentrated hydrochloric acid in a sealed tube in a water-bath. The iso acid dissolved slowly, and there remained an insoluble portion even when the tube was hot. On cooling, more of the same insoluble matter appears, together with clear, colorless crystals of a more soluble compound. These crystals dissolve readily on adding a little water. On evaporating the hydrochloric acid and taking up with water, an insoluble portion remained, which has the following properties: (1) It is fairly insoluble in hot water, but crystallizes from water solution in clear, colorless plates; (2) It is infusible within the range of the thermometer (360°); (3) It is soluble in dilute caustic soda and reprecipitated by hydrochloric acid; it gives off ammonia on boiling with caustic soda, agreeing in all these properties with the infusible diamide.

During the evaporation mentioned, no yellow color appears, nor is the residue yellow, indicating the absence of the iso acid.

On evaporating the filtrate from the insoluble matter also, no yellow color appears, although no hydrochloric acid is now present. On treating the residue from this last evaporation with water, a second insoluble substance appeared, which had the same general appearance as the first. It was obtained in too small quantity to permit of thorough investigation.

Effect of Repeated Evaporation on the Iso Acid.

A portion of the iso acid was repeatedly evaporated with fresh portions of water on a water-bath, in order to test whether the formation of the insoluble substance could be accomplished in this way. The evaporation was repeated six times without result.

The same portion was then evaporated five times with concentrated hydrochloric acid in the same way. This also yielded negative results, no insoluble substance being formed.

Action of Water on the Iso Acid.

On heating a solution of the iso acid in a sealed tube to the temperature of a saturated salt water-bath for several hours, no change was noticed. When a sufficiently concentrated solution is heated in a sealed tube at 220° , crystals separate out on cooling. These are very thin plates which are prolonged in one direction. The amount obtained was too small for an examination.

Action of Dry Air upon the Iso Acid.

A specimen of the iso acid which had been kept over calcium chloride for several weeks, was heated in a current of dry air to 107° .

0.9815 gram gave 0.0893 gram water at this temperature.

	Calculated for	
	$C_6H_4 < \begin{smallmatrix} CO \\ SO_2 \end{smallmatrix} \begin{smallmatrix} [OH \\ [NH_2] \end{smallmatrix}$	
H_2O	8.96	Found. 9.10

No further appreciable loss took place up to 175° . After heating the material was still completely soluble in water. Hence the formation of an insoluble substance is not due to air alone.

Action of Various Gases on the Iso Acid. Steam.

A weighed sample of the anhydrous iso acid was placed in a porcelain boat in a glass tube running through an asbestos covered air-bath. A slow current of steam was now passed through the tube which was kept at a temperature of 175° .

After replacing the steam by dry air, cooling and weighing, a slight loss was indicated, which was not sufficient to account for any deep-seated change. A portion was withdrawn and was found to contain no insoluble matter.

Dry Hydrochloric Acid Gas.

It was thought that possibly this might act as a dehydrating agent. In order to test this, the gas, after passing over the substance, was passed through a weighed U-tube filled with glass beads, which had been moistened with concentrated sulphuric acid. It was found that after heating in a current of the gas from 175° to 190° , neither the U-tube nor the substance changed appreciably in weight. After the operation the substance was as soluble as before.

Moist Hydrochloric Acid Gas at 125° .

This experiment was performed in the same manner as above, and similar results were obtained, *i. e.*, no insoluble matter was formed, nor was there any change in weight. The same sample of the iso acid was used in all these experiments.

The sample which was withdrawn to test the solubility after heating in dry hydrochloric acid gas, was evaporated with concentrated hydrochloric acid. No insoluble matter was formed.

Preparation of the Barium Salt.

Four specimens of the barium salt were prepared in order to test the analytical results given in the former work.

I. Made from the water-extract of the molten mass by rendering it slightly alkaline with ammonia, and precipitating by barium chloride. This was treated with animal charcoal and crystallized twice.

II. The same as above, crystallized a third time.

III. Made from a specimen of the iso acid which had been prepared by treating the barium salt, which had been twice crystallized, with sulphuric acid. The salt, obtained in the regular way from this acid, was twice crystallized.

IV. Made from the flakes which separate from the alcoholic extract of the molten mass.

All the crystallizations mentioned were from hot water. The specimens were all dried on paper. They are identical in solubility and crystal habit, and all the specimens were white.

Analysis of the Barium Salt.

I. 0.5183 gram lost 0.0526 gram at 100° – 110° , and a second loss of 0.0100 gram at 200° – 215° .

II. 0.5137 gram lost 0.0537 gram at 100° – 110° , and a second loss of 0.0085 gram at 200° – 210° .

III. 0.1582 gram lost 0.0193 gram at 200° – 210° .

IV. 0.3315 gram lost 0.0350 at 100° – 110° , a second loss of 0.0033 gram at 150° , and a third of 0.0053 gram at 200° – 220° .

Calculated for ($C_6H_4<\overset{COO}{SO_2}NH_2$) ₂ Ba.		Calculated for ($C_6H_4<\overset{CO}{SO_2}>N$) ₂ Ba.		Specimen.	Found,	
H ₂ O.		H ₂ O.			At lower temperature.	At higher temperature.
+3H ₂ O	9.14	+3H ₂ O	9.73	I	10.15	12.08
+3.5H ₂ O	10.5	+3.5H ₂ O	11.17	II	10.45	12.11
+4H ₂ O	11.82	+4H ₂ O	12.56	III		12.20
				IV	at 150°	
					10.55	11.55 12.16

The salt dries slowly in the air. A specimen which had been exposed about three weeks lost 1.1 per cent. in weight.

Barium Determinations.

I. Anhydrous salt.

(a) 0.2240 gram gave 0.1028 gram BaSO₄.

(b) 0.2473 gram gave 0.1125 gram BaSO₄.

II. (a) Anhydrous salt.

0.1546 gram gave 0.0713 gram BaSO₄.

(b) Hydrus salt.

0.2005 gram gave 0.0821 gram BaSO₄.

III. Anhydrous salt.

0.1395 gram gave 0.0643 gram BaSO₄.

IV. Hydrus salt.

0.1002 gram gave 0.0410 gram BaSO₄.

These results are tabulated below.

Calculated for (C ₅ H ₄ < $\overset{\text{CO}}{\text{SO}_2}$ >N) ₂ Ba.		Specimen.	Found.	
Ba 27.34		I	(a) 26.97	(b) 26.75
		II	(a) 27.11	
		III	27.10	
Calculated for (C ₆ H ₄ < $\overset{\text{CO}}{\text{SO}_2}$ >N) ₂ Ba+4H ₂ O.		II	(b) 24.07	
Ba 23.91		IV	24.06	

These results are sufficient to show that all four specimens are identical.

Sulphur and Nitrogen Estimation.

0.1665 gram gave 0.1570 gram $BaSO_4$. (Liebig).

0.1671 gram gave 0.1564 gram $BaSO_4$.

0.2035 gram gave 10 cc. nitrogen at a temperature of 24° and a pressure of 760 mm. (Dumas).

0.2009 gram gave 10 cc. nitrogen at a temperature of 23° and a pressure of 748 mm.

Calculated for $(C_6H_4<\overset{CO}{SO_2}>N)_2Ba.$		I.	Found. II.	III.	IV.
S	12.77	12.95	12.89		
N	5.59			5.49	5.49

Conductivity Determinations—Preparation of Materials.

It was thought desirable to compare normal parasulphaminebenzoic acid with the iso acid by means of their electric constants. For this purpose the pure sodium salts of the acids as well as the acids themselves are required. The normal acid was prepared as before mentioned.

The sodium salt of the normal acid was prepared by dissolving the acid in a slight excess of sodium hydroxide (from the metal).

The salt was precipitated by alcohol, filtered, washed with alcohol to neutral reaction, crystallized from a mixture of alcohol and water, again washed with alcohol, and finally dried in the air.

Thus prepared, the salt consists of white, micaceous crystals, which are light and bulky. Analysis gave good results for

sodium and showed that the salt contained no water of crystallization.

The sodium salt of the iso acid was prepared by neutralizing the free acid with caustic soda. On adding a large excess of this, the salt is precipitated. Filter, wash to neutral reaction with alcohol, dissolve in water, treat with a small amount of animal charcoal for a few minutes, filter and precipitate with alcohol, filter, wash with alcohol, and dry in the air.

Thus prepared, the salt consists of a mass of very small white crystals.

The yellow color formed on evaporating a solution of the iso acid, which it retains on standing over calcium chloride, is not imparted to the sodium salt, but seems to remain in the mother-liquor. Animal charcoal does not destroy it in a short time.

Analysis of the Sodium Salt.

0.1905 gram lost 0.0296 gram H_2O at 100° .
 0.3465 gram lost 0.0551 gram H_2O at 100° .
 0.1622 gram gave 0.0544 gram Na_2SO_4 .
 0.2813 gram gave 0.0958 gram Na_2SO_4 .

Calculated for
 $C_6H_4<\overset{CO}{SO_2}>N.Na+H_2O$.

H_2O 15.35

I.

15.54

Found.

II.

15.90

Calculated for
 $C_6H_4<\overset{CO}{SO_2}>N.Na$.

Na 11.22

I.

10.86

Found.

II.

11.03

The only available method of purifying the iso acid is the one which has been mentioned, and this gives a yellow colored substance.

The conductivity determinations were made by the method devised by Kohlrausch. The cell constants were determined by means of a fiftieth-normal solution of potassium chloride. The results are given in the following tables.

The Sodium Normal Salt.

Temperature 25°.

v .	First solution. μ .	Second solution. μ .	Third solution. μ .
10	57.41		
20	61.73		
40	64.98		
80	67.33	66.78	
160	69.64	68.35	
320	71.62	70.86	
640	73.45	72.31	70.44
1280			74.91

The second column gives the results obtained by the successive dilution of a tenth-normal solution; the third are of eightieth, etc.

The Sodium Salt of the Iso Acid.¹

v .	First solution.	Second solution.
9.24	62.72	
18.48	70.45	
36.96	75.63	75.63
73.92	80.06	78.96
147.84	84.05	83.55
295.68	86.95	87.32
591.36	89.54	91.61

The results are interpolated in the tables below in order that Ostwald's method for calculating the conductivity at infinite dilution of the sodium salts and the acids might be applied.

The Normal Salt.

v .	μ .	Δ .	μ_{∞} for salt.	μ_{∞} for acid. ²
32	62.38	12	74.38	350.18
64	66.39	10	76.39	352.19
128	68.71	8	76.71	352.51
256	70.84	6	76.84	352.63
512	72.72	4	76.72	352.52

¹ These solutions were made under the assumption that the iso acid was an isomer of parasulphaminebenzoic acid. Afterward the normality was calculated for parabenzoisulphinide. This accounts for the fractions in the v column.

² μ_{∞} for sodium salt + 275.8 = μ_{∞} for acid.

The Iso Salt.

32	74.24	12	86.24	362.04
64	78.87	10	88.87	364.67
128	83.0	8	91.0	366.8
256	86.17	6	92.17	367.97
512	88.90	4	92.90	368.7

It will be observed that the conductivity at infinite dilution for both the normal acid and its sodium salt agree for the different dilutions, but that the figures do not agree in the case of the iso acid. In the latter case the conductivity increases with the time the solution is subjected to the action of the current, a phenomenon which has been observed in the case of other salts.¹ In order to obviate this error a solution was made and its conductivity determined as soon as possible. This gave a result of 368.64 for the acid, but the value increases rapidly, a very dilute solution showing an increase of 1.82 units in five minutes, and 3.68 units in ten minutes.

The Normal Acid.

The normal acid is very insoluble at the temperature of the experiment (25°). The solution used contained 0.0350 gram in 500 cc.

<i>v.</i>	<i>μ.</i>	
2874	224.4	$K^2 = 0.0388$
5748	246.15	$K = 0.0281$

The Iso Acid.

Solution contained 0.1343 gram in 25 cc.

<i>v.</i>	<i>μ.</i>
34.092	323.27
68.184	331.9
136.368	341.43
272.736	359.1
545.472	369.3
1090.944	376.4

¹ Dissertation by McKay.

$$^2 K = \frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{v\left(1 - \frac{\mu_v}{\mu_\infty}\right)}$$

If we compare the limiting value of the conductivity of the iso acid, as calculated from its sodium salt, with the results obtained by using the acid itself, we see that the latter values exceed the former at a relatively small dilution. This would indicate the formation in solution of simpler molecules having a greater number of ions, and consequently the validity of the results in determining the coefficient of affinity (K) is destroyed.

Action of Hydrochloric Acid on the Barium Salt of the Iso Acid.

A small amount of the barium salt was boiled seven hours with dilute hydrochloric acid (sp. gr. 1.12). On standing over night, crystals separate out which dissolve on heating; on cooling, they again appear, and are redissolved without difficulty. On repeating the operation, they all dissolve with the exception of a few particles, which increase in number on boiling until a good yield is obtained.

The substance is crystalline and fairly insoluble; it contains barium, but no nitrogen could be detected on fusion with metallic sodium. The properties of the substance resemble those of acid barium parasulphobenzoate, but the amount obtained was too small to be tested. For the sake of obtaining more of this substance, a larger amount of the barium salt was treated as above, the acid being of about the concentration, and the solution containing approximately the same amount of barium per unit volume. The boiling was continued for eighteen hours, and the salt was repeatedly crystallized out and redissolved, but the insoluble substance did not appear. Instead of this, the crystals which are formed on cooling from time to time, gradually lose the characteristic silky form of the barium iso salt, coming out finally as very thin flakes which, after filtering, have a white micaceous appearance. The salt gives off ammonia when fused with caustic potash. After recrystallizing, the salt comes out in very thin, clear, colorless plates, which are prolonged in one direction. An analysis gave the following results:

0.2865 gram lost 0.0279 gram H_2O at 100° – 120° .

0.0998 gram gave 0.0389 gram $BaSO_4$.

Above 200° there is a second slight loss in weight which is accompanied by the formation of a slight sublimate.

	I.	II.
Ba.....	22.92	
H ₂ O		9.74

This would give 25.39 per cent. barium in the anhydrous salt. The theoretical per cent. of barium in the barium salt of parasulphaminebenzoic acid is 25.51 per cent.

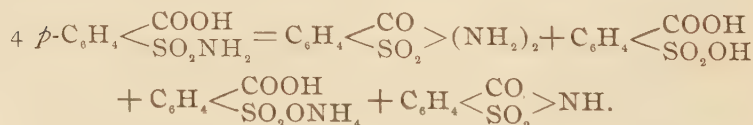
A lack of material and of time prevented a further investigation of these compounds.

Conclusion.

From the analyses of the sodium and barium salts of the iso acid, it appears that the acid is *not* isomeric with parasulphaminebenzoic acid, but corresponds to this less one molecule of water.

The composition and properties of the magnesium and potassium salts of the acid derived from the infusible diamide of parasulphobenzonic acid, show that both are salts of an acid isomeric with parasulphaminebenzoic acid, or an isoparasulphaminebenzoic acid in reality. The facts known with regard to these salts indicate, but do not show conclusively, that in the infusible diamide, both nitrogen atoms may be in combination with carbon, and that the acid really isomeric with parasulphaminebenzoic acid may be paracarbaminebenzenesulphonic acid.

If the anhydride formula for Muckenfuss' iso acid be accepted, the action of heat upon parasulphaminebenzoic acid may be thus represented :



It will be remembered that the products actually obtained, and the only ones obtained, by heating the parasulphaminebenzoic acid, are those represented in this equation, that is to say, the infusible diamide, free parasulphobenzonic acid, acid ammonium parasulphobenzoate, and the iso acid.

BIOGRAPHICAL.

WILLIAM BULL STODDARD was born in Burlington, Vermont, August 24, 1872. In 1878 his parents removed to Boulder, Colorado. His early education was received in the public schools of that place. When sixteen years of age he entered the Colorado State Preparatory School, going from there to the State University of Colorado, where he received the degree of Bachelor of Science in 1894. Since then he has been enrolled in the Johns Hopkins University as a graduate student in chemistry, geology, and mineralogy.

